Effects of Hydrostatic Pressure on the Cloud Point of Surface-Active Agent (Commemoration Issue Dedicated to Professor Rempei Gotoh On the Occasion of his Retirement)

AUTHOR(S):

Suzuki, Keizo; Tsuchiya, Masao

Bull. Inst. Chem. Res., Kyoto Univ., Vol. 47, No. 4, 1969

Effects of Hydrostatic Pressure on the Cloud Point of Surface-Active Agent*

Keizo SUZUKI and Masao TSUCHIYA**

Received May 28, 1969

The effects of hydrostatic pressure on the cloud point of aqueous solution of polyoxyethylene nonylphenyl ether were examined in the range up to 5000 atm. A maximum appears at about 1000–2000 atm in the cloud point *vs.* pressure curve. This fact shows that the low pressure below 1000–2000 atm is favorable to disperse the solute molecules and the high pressure above 1000–2000 atm is favorable to assemble the solute molecules. This suggests to us that the low pressure below 1000–2000 atm enhances to form hydrogen bonds between surface active agent and water molecules, and then tends to disrupt the assembly of hydrocarbon moiety, so-called "hydrophobic bonds". The high pressure above 1000–2000 atm works on the opposite direction.

I. INTRODUCTION

There are several evidences that the effects of hydrostatic pressure on some proteins in the range 1–2000 atm are inverted at the pressure above about 2000 atm.[1] In order to clarify this curious inversion it is necessary to get the informations about the effects of pressure on some model systems. Surface-active agents may be regarded as the model of proteins in viewpoint of having hydrophilic and hydrophobic groups in a molecule. Some investigations of pressure effect on the critical micelle concentration (c.m.c.) of ionic surface-active agents have been performed recently.[2] The results show that the c.m.c. initially increases with increasing of pressure and then this positive trend inverts at about 1000 atm. This unusual effect of pressure in the simple chemical system has not been explained explicitly, yet. This curious inversion seems to be related to that found in proteins.

In this report some results of the effect of pressure on the cloud point of nonionic surface-active agent will be presented, and the influences of pressure on hydrogen bonds and hydrophobic bonds will be discussed. Any investigation on cloud point under high pressure has not been found in literatures.

II. EXPERIMENTAL

1. Material

Polyoxyethylene nonylphenyl ether ($C_9H_{19}C_6H_4O(CH_2CH_2O)_{8.2}H$, PNE) was taken as a sample, which was donated by Daiichi Pharmaceutical Campany.

* A part of the results in this report was presented at the 20th Annual Meeting of Chemical Society of Japan, Tokyo (1967), and in *Rev. Phys. Chem. Japan*, 38, 63 (1968).

** 鈴木 啓三, 土屋 正夫: Department of Chemistry, Faculty of Science and Engineering, Ritsumeikan University, Kyoto.

The c.m.c. observed from surface tension was 5×10^{-5} moles/liter at 25°C. This value is comparable with the data of Hsiao *et al.*[3]

2. Apparatus and Procedure

The detail of high pressure vessel with optical windows was reported elsewhere.[4] The cloud points were decided by observing the appearance and disappearance of turbidity in the course of increasing and decreasing the temperature at a given pressure, and in the course of increasing and decreasing the pressure at a given temperature. The errors of experiments were within ±1.0°C in temperature, and ±100 atm in pressure.

III. RESULTS AND DISCUSSION

Figure 1 is the phase diagram obtained at atmospheric pressure. It is interesting to note that Fig. 1 resembles the partial miscible solbility curve which has a lower critical solution temperature (LCST). Every organic compound having the LCST, for example, pyridine, piperidine, imine, glycol, amine, ketone, *etc.* and their derivatives,[5] contains both hydrophilic group and hydrophobic group in the molecule as well as surface active agents have.

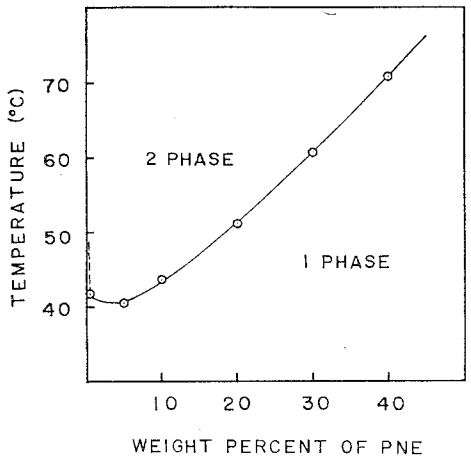

Fig. 1. Phase diagram of PNE-water system at 1 atm.

Figure 2 shows the results of the effect of pressure on the cloud point at various concentrations. Each curve has a maximum at about 1000–2000 atm. As the concentration of surface-active agent increases, the cloud point *vs.* pressure curve shifts towards the higher temperature and the maximum becomes broad. The similar patterns to Fig. 2 have been also found in the c.m.c. *vs.* pressure curve[2] and the LCST *vs.* pressure curve.[6] All these results are consistent with each other in the fact that the low pressure below 1000–2000 atm is favorable to the dispersion of solute molecules in water, but the high pressure above 1000–2000 atm is unfavorable to the dispersion.

The volume change in the transfer of hydrocarbons from nonpolar solvents to water is negative (about −20 ml/mole).[7] This indicates that hydrostatic

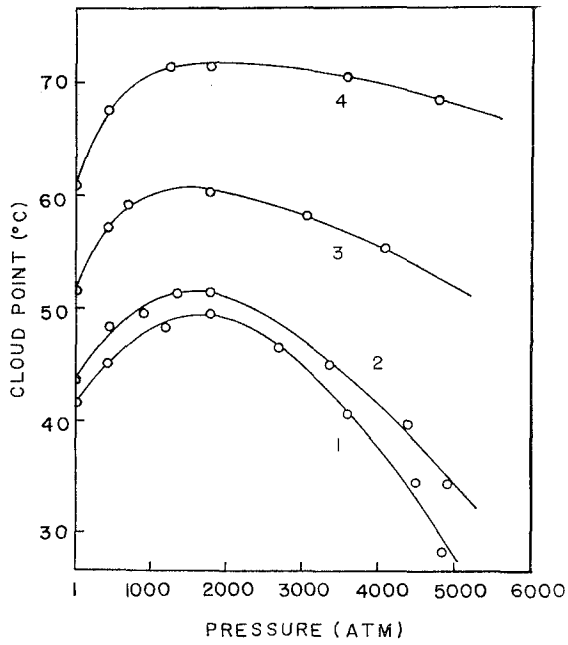

Fig. 2. Effect of pressure on the cloud point of PNE-water system.
Weight percent of PNE
1: 0.05 2: 10.0 3: 20.0 4: 30.0

compression favors the disruption of the assembly of hydrocarbon molecules, so-called "hydrophobic bonds". On the other hand, it has been confirmed from the spectrophotometric investigations under high pressure that the formation of hydrogen bonds is enhanced by increasing the pressure (association of alcohols in nonpolar solvents ;[8] hydrogen bond between phenol and dioxane in *n*-hexane[9]). That is, the effects of pressure on the formation of hydrogen bond are quite opposite with those on the formation of hydrophobic bonds. The increase of cloud point may be assumed to be caused by the disruption of hydrophobic bonds between the solute molecules and the formation of hydrogen bonds between solute and solvent molecules by the application of pressure.

The inversion above 1000-2000 atm seems to reflect the change of water structure under high pressure.[10] The decrease of solubility above 1000-2000 atm will be plausibly explained by supposing the formation of hydrophobic bonds and the disruption of hydrogen bonds between solute and solvent molecules, because the hydrogen bonds between water molecules are strengthened owing to the change of water structure. It will be reasonable to assume that the inversion of the pressure effects on proteins may be ascribed to the same reason.

ACKNOWLEDGMENT

One of the authors (K. Suzuki) would like to express his sincere thanks to Prof. R. Gotoh who encouraged him to take an interest in the field of colloid chemistry.

REFERENCES

(1) F. H. Johnson, H. Eyring and M. Polissar, "The Kinetic Basis of Molecular Biology", John Wiley & Sons, Inc., New York, 1954, pp. 286-368; K. Suzuki, *Rev. Phys. Chem. Japan*, 28, 24 (1958); K. Suzuki and Y. Miyosawa, *J. Biochem. Tokyo*, 57, 116 (1965); K. Miyagawa, K. Sannoe and K. Suzuki, *Arch. Biochem. Biophys.*, 106, 467 (1964).
(2) S. D. Hamann, *J. Phys. Chem.* **66**, 1359 (1962); R. F. Tuddenham and A. E. Alexander, *ibid.*, **66**, 1839 (1962); J. Osugi, M. Sato and N. Ifuku, *J. Chem. Soc. Japan*, 87, 329 (1966).
(3) L. Hsiao, H. N. Dunning and P. B. Lorenz, *J. Phys. Chem.*, **60**, 657 (1956).
(4) K. Suzuki, Y. Miyosawa and C. Suzuki, *Arch. Biochem. Biophys.*, **101**, 225 (1963).
(5) A. W. Francis, "Critical Solution Temperature", Am. Chem. Soc., Washington, D. C., 1961, p. 209.
(6) G. Schneider, *Z. Phys. Chem. N. F.*, 37, 333 (1963); *ibid.*, 39, 187 (1963).
(7) W. Kauzmann, *Advan. Protein Chem.*, **14**, 1 (1959).
(8) E. Fishman and H. D. Drickamer, *J. Chem. Phys.*, **24**, 548 (1956), J. Osugi and Y. Kitamura, *Rev. Phys. Chem. Japan*, 35, 25 (1965).
(9) K. Suzuki and M. Tsuchiya, Preprint of the 9th Symposium on High Pressure, p. 95 (1967).
(10) A. W. Lawson and A. J. Hughes, "High Pressure Physics and Chemistry", Vol. 1, Edited by R. S. Bradley, Academic Press, New York, 1963, pp. 207-225.